(19) Japan Patent Office (JP)

(11) Patent Application Publication No.

(12) Public Patent Announcement (A) **Pat Open Hei 4-238812**

(43) Publication Date: August 26, 1992

(51) Int. Cl.[5]		ID Code	Internal Cl. No.	FI	Technology Display Section
C 01 F	11/18	A	9040-4G		
C 08 K	3/26	KAF	7167-4J		
	7/16	KCL	7167-4J		

Examination request: Not requested Number of patent claims: 2 (Altogether 17 pages)

(21) Application No.: Pat App Hei 2-415863

(22) Application Date: December 28, 1990

(71) Applicant: 000174541
Sakai Chemical Industry Co., Ltd.
1-1-23, Ebisuno-cho-Nishi, Sakai City, Osaka

(72) Inventor: Akira Kotone
c/o Sakai Chemical Industry Co., Ltd.
5-1, Ebisujima-cho, Sakai City, Osaka

(72) Inventor: Masayoshi Hirota
c/o Sakai Chemical Industry Co., Ltd.
5-1, Ebisujima-cho, Sakai City, Osaka

(72) Inventor: Katsutoshi Shibata
c/o Sakai Chemical Industry Co., Ltd.
5-1, Ebisujima-cho, Sakai City, Osaka

(74) Agent: Hirokatsu Kamei, Patent attorney (and two others)

(Continued to the last page)

(54) [Title of Invention]

Spherical calcium carbon and its manufacturing method.

(57) [Abstract]

[Construction]

Calcium chloride and hydrogen carbonate or carbonate are reacted in the presence of a specific phosphate compound of a specified amount to obtain spherical calcium carbonate containing a vaterite form of 30 % or more.

[Efficacy]

Because it is stable in the air, it is excellent in dispersibility, fillability, and smoothness, and can be used preferably as an additive and filler.

[Scope of Patent Claims]

[Claim 1]

Spherical calcium carbonate characterized by containing a vaterite form of 30 % or more.

[Claim 2]

In a calcium carbonate manufacturing method where calcium carbonate and hydrogen carbonate and/or carbonate are reacted in a water-system solvent, a spherical calcium carbonate manufacturing method characterized by having at least one kind of phosphate compounds expressed by the following general formulae (I)~(VIII) exist in the ratio of 3 wt% or more relative to the theoretical yield of generated calcium carbonate in the water-system solvent.

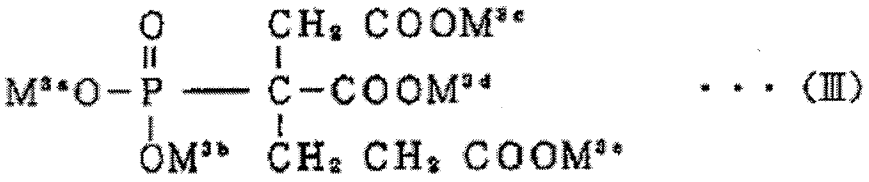
M_2PO_{31} (I)

(In the formula, M indicates a hydrogen atom or an alkali metal, and n is 1 or an integer larger than 1.)

(MPO_3) (II)

(In the formula, M is the same as the above, and m is an integer 3 or 4.)

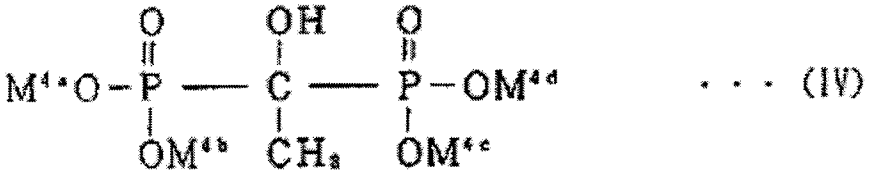
[Chem 1]



(III)

(In the formula, M^3, M^3, M^3, M^3, and M^3 are identical or different, being a hydrogen atom or an alkali metal.)

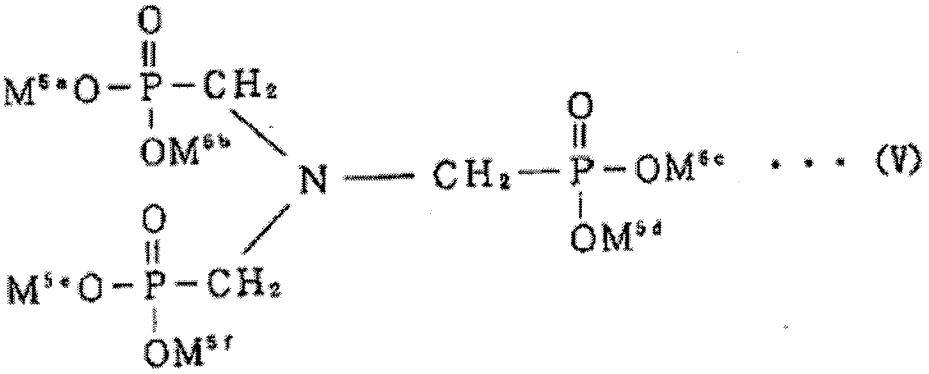
[Chem 2]



(IV)

(In the formula, M^4, M^4, M^4, and M^4 are identical or different, being a hydrogen atom or an alkali metal.)

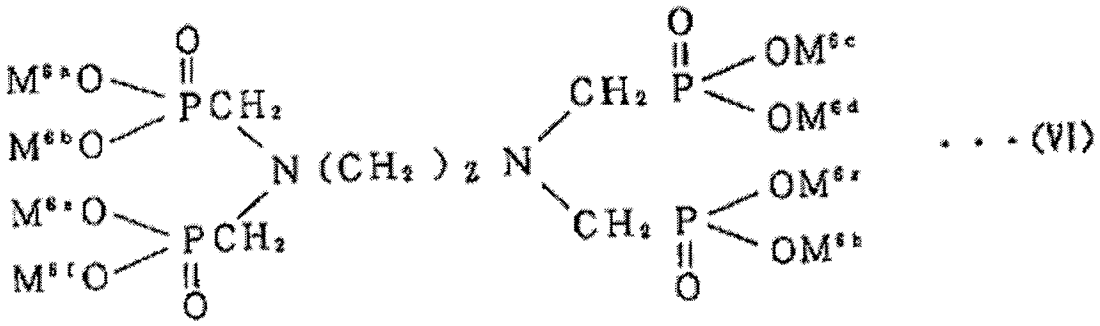
[Chem 3]



(V)

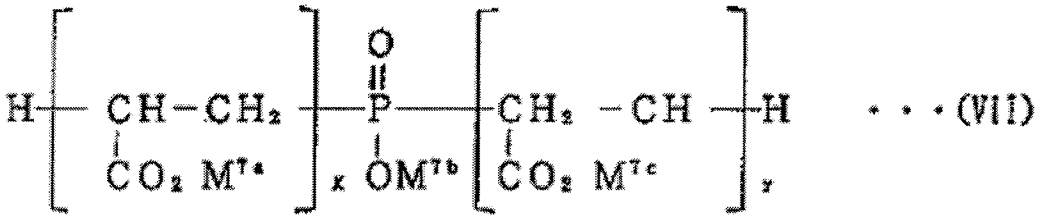
(In the formula, M^5, M^5, M^5, M^5, M^5, and M^5 are identical or different, being a hydrogen atom or an alkali metal.)

[Chem 4]



(VI)

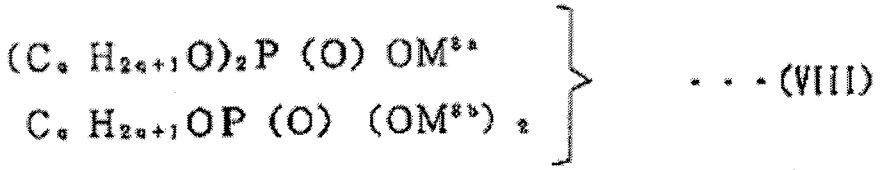
(In the formula, M^6, M^6, M^6, M^6, M^6, M^6, M^6, and M^6 are identical or different, being a hydrogen atom or an alkali metal, and z is an integer of 1~4.)



[Chem 5]

(VII)

(In the formula, M^7, M^7, and M^7 are identical or different, being a hydrogen atom or an alkali metal, and the sum of x and y is 4~16.)



[Chem 6]

(VIII)

(In the formula, M^8 and M^8 are identical or different, being a hydrogen atom or an alkali metal, and q is an integer of 1~18.)

[Detailed Explanation of the Invention]

[0001]

[Field of Industrial Application]

The present invention relates to a manufacturing method of spherical calcium carbonate, and specifically relates to a manufacturing method of spherical calcium carbonate which can be utilized as additives, fillers, etc. for ink, rubber, synthetic resin, paint, paper, medicine, food, cosmetics, electronic industry, ceramics, etc.

[0002]

[Prior Art Technology]

Among the polymorphs of calcium carbonate crystal are the calcite form of the hexagonal system (rhombohedron), the aragonite form of the orthorhombic system (acicula), and the vaterite form of the pseudo-hexagonal system (spherule). Among these, although calcite form and aragonite form exist in nature, it is believed that the vaterite form does not exist in nature and is unstable. Namely, among the crystal forms of calcium carbonate, while the calcite form is stable, the aragonite form and the vaterite form are metastable, and especially the vaterite form has a nature that it is easily transformed into the calcite form or the aragonite form once it has come into contact with water.

[0003]

There are following three kinds of calcium carbonate manufacturing methods known in general:

(1) A method where calcium chloride and carbonate (such as sodium carbonate) or hydrogen carbonate are reacted.

(2) A method where calcium hydroxide and carbonate or hydrogen carbonate are reacted.

(3) A method where calcium hydroxide and carbonate gas are reacted.

Among these methods, the most widely adopted method is (3).

[0004]

[Problems overcome by the Invention]

However, calcium carbonate manufactured by the methods of (1)~(3) are either the calcite form or includes the aragonite form, and it was extremely difficult to obtain stably spherical calcium carbonate of the vaterite form. The reason for this is that, as stated above the vaterite form is extremely unstable and is easily transformed into the calcite form or the aragonite form.

[0005]

However, because various kinds of characteristics of calcium carbonate such as fillability, dispersibility, and polishability are improved and preferred characteristics are added by making calcium carbonate powder spherical, providing spherical calcium carbonate has been conventionally demanded in many fields. Therefore, although there is a proposal to treat the surface of calcium carbonate of the vaterite form with higher fatty acid to stabilize it (Laid Open Patent Sho 55-95617), there is a problem that its dispersibility to water becomes worse because it is treated with higher fatty acid. Also, in manufacturing calcium carbonate through an aqueous solution reaction of calcium salt and carbonate, although there is a proposal to react them by adding a bivalent metal ion other than calcium (Pat Pub Sho 63-5331 Public Report), no sufficient stabilizing effect has been obtained. Furthermore, although there is also a proposal to treat spherical vaterite-form calcium carbonate at high temperature to transform it into calcite while keeping its spherical form (Pat Pub Sho 63-10923 Public Report), there are problems such as adhesion of particles and cost increase due to the high-temperature treatment.

[0006]

Therefore, an objective of the present invention is to provide spherical calcium carbonate including the stable vaterite form and its manufacturing method.

[0007]

[Problem Resolution Means]

As a result of repeating zealous research in order to achieve the objective, the inventors discovered the fact that spherical calcium carbonate containing the vaterite form of 30 % or more can achieve the objective and thereby completed the present invention. In order to manufacture such spherical calcium carbonate of the present invention, in reacting calcium chloride and hydrogen carbonate or/and carbonate in a water-system solvent, at least one kind of phosphate compounds expressed in the general formulae (I)~(VIII) is permitted in an aqueous solvent in a ratio of 0.3 wt% or higher relative to the theoretical yield of generated calcium carbonate.

[0008]

(I)

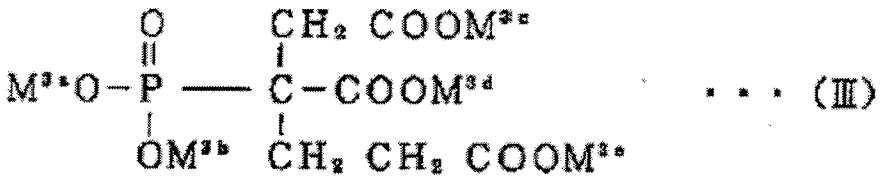
(In the formula, M indicates a hydrogen atom or an alkali metal, and n is 1 or an integer larger than 1.)

(II)

(In the formula, M is the same as the above, and m is an integer 3 or 4.)

[0009]

[Chem 7]

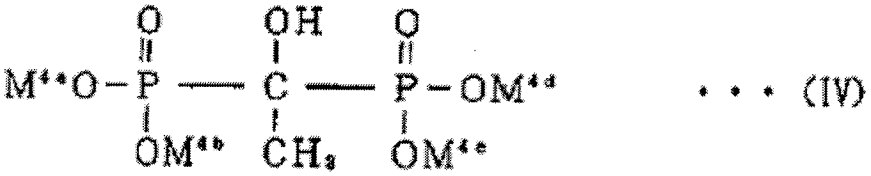


(III)

(In the formula, M^3, M^3, M^3, M^3, and M^3 are identical or different, being a hydrogen atom or an alkali metal.)

[0010]

[Chem 8]

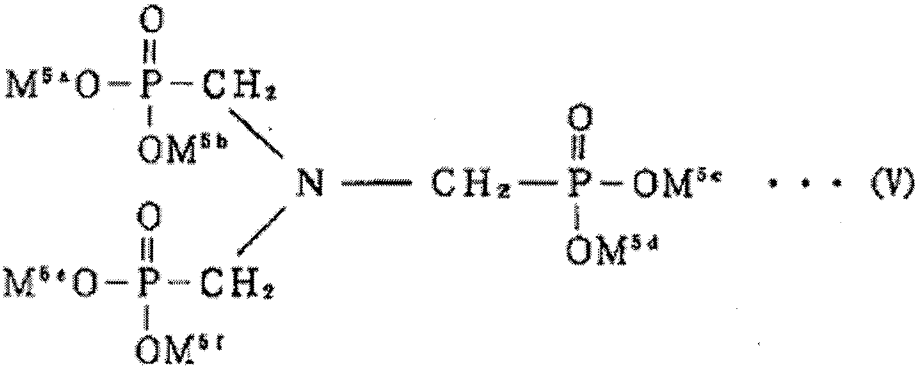


(IV)

(In the formula, M^4, M^4, M^4, and M^4 are identical or different, being a hydrogen atom or an alkali metal.)

[0011]

[Chem 9]

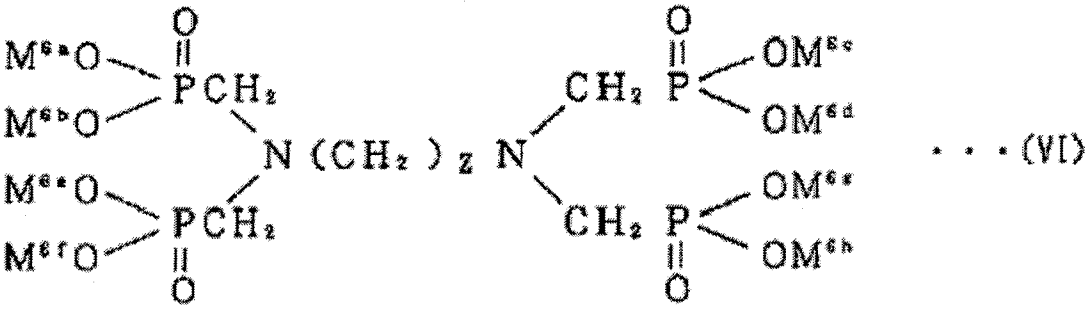


(V)

(In the formula, M^5, M^5, M^5, M^5, M^5, and M^5 are identical or different, being a hydrogen atom or an alkali metal.)

[0012]

[Chem 10]

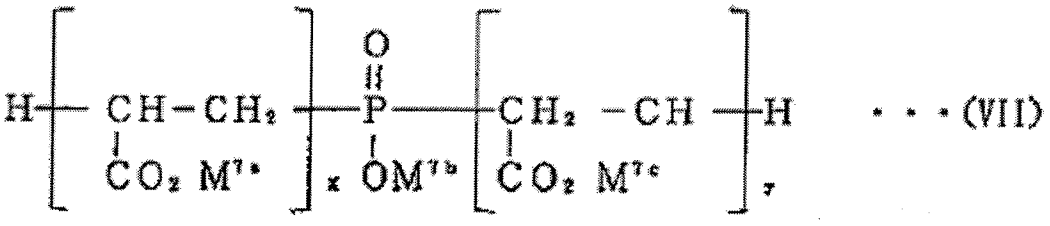


(VI)

(In the formula, M^6, M^6, M^6, M^6, M^6, M^6, M^6, and M^6 are identical or different, being a hydrogen atom or an alkali metal, and z is an integer of 1~4.)

[0013]

[Chem 11]



(VII)

(In the formula, M^7, M^7, and M^7 are identical or different, being a hydrogen atom or an alkali metal, and the sum of x and y is 4~16.)

[0014]

[Chem 12]

$$\left.\begin{array}{l}(C_qH_{2q+1}O)_2P(O)OM^{8a}\\ C_qH_{2q+1}OP(O)(OM^{8b})_2\end{array}\right\} \quad \cdots (VIII)$$

(VIII)

(In the formula, M^8 and M^8 are identical or different, being a hydrogen atom or an alkali metal, and q is an integer of 1~18.) M in the phosphate compounds expressed in the general formulae (I) and (II) includes the case where one part is alkali metals and the other hydrogen atoms as well as the case where all are alkali metals.

[0015]

The reaction to obtain the spherical calcium carbonate of the present invention has the reaction of calcium carbonate and hydrogen carbonate and/or carbonate as its basis. Listed as hydrogen carbonate is sodium hydrogen carbonate or potassium hydrogen carbonate. Also, listed as carbonate is sodium carbonate or potassium carbonate. The reaction ratio (molar ratio) of the two ingredients in the case of calcium carbonate : hydrogen carbonate is in the range of 1:0.5 ~ 1:2 to be appropriate, and preferably 1:2. In the case of calcium chloride : carbonate should be in the range of 1:0.5 ~ 1:2 to be appropriate, and preferably 1:1.

[0016]

Reaction is performed by preparing each aqueous solution of the two ingredients, adding the solution of one ingredient to the solution of the other ingredient, and stirring it for a specified time. At this time, the phosphate compounds expressed in the general formulae (I)~(VIII) are dissolved in an aqueous solution before adding the other ingredients. Such phosphate compounds are believed to act as so-called a crystal modifier, which can generate spherical calcium carbonate with precedence.

[0017]

The compounds expressed by the general formulae (I)~(VIII) are concretely shown as the phosphate compounds. Listed as the phosphate compounds expressed by the general formula (I) or (II) are linear or cyclic phosphate compounds such as orthophosphoric acid, sodium orthophosphate, potassium orthophosphate, pyrophosphoric acid, sodium pyrophosphate, potassium pyrophosphate, tripolyphophoric acid, sodium tripolyphosphate, potassium tripolyphosphate; trimetaphosphoric acid, sodium trimetaphosphate, potassium trimetaphosphate, tetrametaphosphoric acid, potassium tetrametaphosphate, sodium tetrametaphosphate, hexametaphosphoric acid, sodium hexametaphosphate, and potassium hexametaphosphate for example.

[0018]

Also, listed as the phosphonic acid (or its salt) and phosphinic acid (or its salt) expressed by the general formula (III), (IV), (V), (VI), and (VII) are 2-phophonobutane tricarboxylic acid-1,2,4, 2-phosphonobutane tricarboxylic acid-1,2,4-monosodium salt, 2-phosphonobutane tricarboxylic acid-1,2,4-monopotassium salt, 2-phosphonobutane tricarboxylic acid-1,2,4-disodium salt, 2-phosphonobutane tricarboxylic acid-1,2,4-dipotassium salt, 2-phosphonobutane tricarboxylic acid-1,2,4-trisodium salt, 2-phosphonobutane tricarboxylic acid-1,2,4-tripotassium salt, 2-phosphonobutane tricarboxylic acid-1,2,4-tetrasodium salt, 2-phosphonobutane tricarboxylic acid-1,2,4-tetrapotassium salt; 1-hydoxyethylidene-1,1-diphosphonic acid, 1-hydoxyethylidene-1,1-diphosphonic acid-monosodium salt, 1-hydoxyethylidene-1,1-diphosphonic acid-monopotassium salt, 1-hydoxyethylidene-1,1-diphosphonic acid-disodium salt, 1-hydoxyethylidene-1,1-diphosphonic acid-dipotassium salt, 1-hydoxyethylidene-1,1-diphosphonic acid-trisodium salt, 1-hydoxyethylidene-1,1-diphosphonic acid-tripotassium salt; aminotri(methylene phosphonic acid), aminotri(methylene phosphonic acid)-monosodium salt, aminotri(methylene

phosphonic acid)-monopotassium salt, aminotri(methylene phosphonic acid)-disodium salt, aminotri(methylene phosphonic acid)-dipotassium salt, aminotri(methylene phosphonic acid)-trisodium salt, aminotri(methylene phosphonic acid)-tripotassium salt, aminotri(methylene phosphonic acid)-tetrasodium salt, aminotri(methylene phosphonic acid)-tetrapotassium salt, aminotri(methylene phosphonic acid)-pentasodium salt, aminotri(methylene phosphonic acid)-pentapotassium salt; ethylene diamine tetra (methylene phosphonic acid), ethylene diamine tetra (methylene phosphonic acid)-monosodium salt, ethylene diamine tetra (methylene phosphonic acid)-monopotassium salt, ethylene diamine tetra (methylene phosphonic acid)-disodium salt, ethylene diamine tetra (methylene phosphonic acid)-dipotassium salt, ethylene diamine tetra (methylene phosphonic acid)-trisodium salt, ethylene diamine tetra (methylene phosphonic acid)-tripotassium salt, ethylene diamine tetra (methylene phosphonic acid)-tetrasodium salt, ethylene diamine tetra (methylene phosphonic acid)-tetrapotassium salt, ethylene diamine tetra (methylene phosphonic acid)-pentasodium salt, ethylene diamine tetra (methylene phosphonic acid)-pentapotassium salt, ethylene diamine tetra (methylene phosphonic acid)-hexasodium salt, ethylene diamine tetra (methylene phosphonic acid)-hexapotassium salt; sodium bis(poly-2-carboxyethyl) phosphinate, potassium bis(poly-2-carboxyethyl) phosphinate, etc. for example.

[0019]

The phosphate compound expressed by the general formula (VIII) is a mixture of dialkylester and monoalkylester, which can be obtained industrially in such a mixture form. Specifically, listed are methyl acid phosphate, methyl acid phosphate-monosodium salt, methyl acid phosphate-monopotassium salt, methyl acid phosphate-disodium salt, methyl acid phosphate-dipotassium salt; ethyl acid phosphate, ethyl acid phosphate-monosodium salt, ethyl acid phosphate-monopotassium salt, ethyl acid phosphate-disodium salt, ethyl acid phosphate-dipotassium salt; isopropyl acid phosphate, isopropyl acid phosphate-monosodium salt, isopropyl acid phosphate-monopotassium salt, isopropyl acid phosphate-disodium salt, isopropyl acid phosphate-dipotassium salt; butyl acid phosphate, butyl acid phosphate-disodium salt, butyl acid phosphate-dipotassium salt; 2-ethylhexyl acid phosphate, 2-ethylhexyl acid phosphate-monosodium salt, 2-ethylhexyl acid phosphate-monopotassium salt, 2-ethylhexyl acid phosphate-disodium salt, 2-ethylhexyl acid phosphate-dipotassium salt, etc.

[0020]

The amount of phosphate compounds to add is in the ratio of 0.3 wt % or more relative to theoretical yield of generated calcium carbonate, preferably 0.3~50 wt%, and even more preferably 0.6~20 wt%. When the amount of phosphate compound to add does not reach 0.3 wt%, because mixing of rhombohedron calcium carbonate in the generated spherical calcium carbonate is recognized, it is not preferred.

[0021]

It is appropriate to perform the reaction of calcium chloride and hydrogen carbonate and/or carbonate under the existence of phosphate compound at 0~60°C, preferably 10~40°C. Also, the appropriate reaction time is about 5~30 min, preferably about 10~20 min. The pH of the reaction liquid after the reaction was 6~8 in the case of hydrogen carbonate, and 8~10 in the case of carbonate.

[0022]

After the reaction, the product is filtered, washed with water, and dried to obtain the target calcium carbonate. This material has an average particle size (median size) in the range of about 4~8 μm, and 50 % or more particles exist in the particle size range being about 2~12 μm. The calcium carbonate obtained in this way is nearly a spherical material containing the vaterite form by at least 30 % or more according to the result of an X-ray diffraction. The spherical calcium carbonate obtained this way is stable in the air at the room temperature over a long period.

[0023]

Note that the spherical shape referred to in the present invention is a concept which includes that close to an ellipsoid other than a perfect spherical shape. Also, the reaction may be performed in a water-system medium where a solvent such as low-grade alcohol is mixed with water other than an aqueous solution.

[0024]

[Actions]

The spherical calcium carbonate of the present invention is excellent in stability in the air and can maintain its spherical form over a long period. Also, in the method of the present invention, because the reaction is performed under the existence of a specific phosphate compound of a specified amount, the phosphate compound works as a crystal modifier, and stable spherical calcium carbonate can be obtained economically with a high yield.

[0025]

[Embodiments]

Next, the spherical calcium carbonate of the present invention and its manufacturing method are explained according to the embodiments.

Embodiment 1

Sodium trimetaphosphate 30 mg was added so that it becomes 0.3 wt% relative to the theoretical yield of generated calcium carbonate. $CaCl_2$ 0.5 mol/l aqueous solution 200 ml was put in a 100 ml beaker, and Na2CO3 0.5 mol/l aqueous solution 200 ml was added to this aqueous solution as it is stirred with a magnetic stirrer at the room temperature. After mixing, stirring was further continued for 10 minutes, the reaction product was filtered with a membrane filter, cleaned well with water, and dried at about 120°C, obtaining calcium carbonate.

Embodiment 2

Calcium carbonate was obtained in the same way as in the embodiment 1 except for adding sodium trimetaphosphate 60 mg (0.6 wt% relative to theoretical yield of generated calcium carbonate).

Embodiment 3

Calcium carbonate was obtained in the same way as in the embodiment 1 except for adding sodium trimetaphosphate 2000 mg (20 wt% relative to theoretical yield of generated calcium carbonate).

Embodiment 4

Calcium carbonate was obtained in the same way as in the embodiment 1 except for adding sodium trimetaphosphate 5000 mg (50 wt% relative to theoretical yield of generated calcium carbonate).

Embodiment 5

Calcium carbonate was obtained in the same way as in the embodiment 1 except for adding sodium trimetaphosphate 60 mg (0.6 wt% relative to theoretical yield of generated calcium carbonate) in place of sodium trimetaphosphate.

Embodiment 6

Calcium carbonate was obtained in the same way as in the embodiment 1 except for adding sodium tripolyphosphate 60 mg (0.6 wt% relative to theoretical yield of generated calcium carbonate) in place of sodium trimetaphosphate.

Embodiment 7

Calcium carbonate was obtained in the same way as in the embodiment 1 except for adding 2-phosphonobutane tricarboxyl acid-1,2,4 60 mg (0.6 wt% relative to theoretical yield of generated calcium carbonate) in place of sodium trimetaphosphate.

Embodiment 8

Calcium carbonate was obtained in the same way as in the embodiment 1 except for adding 1-hydroxyethylidene-1,1-diphosphonic acid 60 mg (0.6 wt% relative to theoretical yield of generated calcium carbonate) in place of sodium trimetaphosphate.

Embodiment 9

Calcium carbonate was obtained in the same way as in the embodiment 1 except for adding aminotri(methylene phosphonic acid) 60 mg (0.6 wt% relative to theoretical yield of generated calcium carbonate) in place of sodium trimetaphosphate.

Embodiment 10

Calcium carbonate was obtained in the same way as in the embodiment 1 except for adding ethylene diamine tetra(methylene phosphonic acid) 60 mg (0.6 wt% relative to theoretical yield of generated calcium carbonate) in place of sodium trimetaphosphate.

Embodiment 11

Calcium carbonate was obtained in the same way as in the embodiment 1 except for adding sodium bis(poly-2-carboxyethyl) phosphinate 60 mg (0.6 wt% relative to theoretical yield of generated calcium carbonate) in place of sodium trimetaphosphate.

Embodiment 12

Calcium carbonate was obtained in the same way as in the embodiment 1 except for adding sodium methyl acid phosphate 60 mg (0.6 wt% relative to theoretical yield of generated calcium carbonate) in place of sodium trimetaphosphate.

Embodiment 13

Calcium carbonate was obtained in the same way as in the embodiment 1 except for adding sodium butyl acid phosphate 60 mg (0.6 wt% relative to theoretical yield of generated calcium carbonate) in place of sodium trimetaphosphate.

Embodiment 14

Calcium carbonate was obtained in the same way as in the embodiment 2 except for adding sodium hydrogen carbonate 1.0 mol/l aqueous solution 200 ml as carbonate in place of sodium carbonate.

Embodiment 15

Calcium carbonate was obtained in the same way as in the embodiment 1 except for adding sodium trimetaphosphate 10000 mg (100 wt% which is the same amount with theoretical yield of generated calcium carbonate).

Comparison example

Calcium carbonate was obtained in the same way as in the embodiment 1 except for adding sodium trimetaphosphate 10 mg (0.1 wt% relative to theoretical yield of generated calcium carbonate).

[0026]

The yield, average particle size, specific surface area, vaterite ratio of calcium carbonate obtained in each of the embodiments and the comparative example are listed in Table 1. The average particle size is in the median size, and the specific surface area was acquired by the BET method. Note that the particle size was measured using a laser diffraction particle size distribution meter "LA-500" manufactured by Horiba Factory. Also, the vaterite ratio was computed according to the following formula by M. S. Rao, Bull. Chem. Soc. Japan, 46, 1414 (1973).

[0027]

$$\text{Vaterite ratio } F(v) = f(v) \times 100,$$

where

$$f(v) = 1 - I_{104(C)} / (I_{110(V)} + I_{112(V)} + I_{114(V)} + I_{104(C)}).$$

In the formula,

$I_{104(C)}$ is the X-ray diffraction intensity at the 104 plane of calcite,
$I_{110(V)}$ is the X-ray diffraction intensity at the 110 plane of calcite,
$I_{112(V)}$ is the X-ray diffraction intensity at the 112 plane of calcite,
$I_{114(V)}$ is the X-ray diffraction intensity at the 114 plane of calcite.

[0028]

[Table 1]

Embodiment No.	Yield (g)	Average particle size (μm)	Specific surface ratio (m^2/g)	Vaterite ratio (%)
1	10.2	8.6	9.1	33.0
2	10.1	5.8	5.8	77.0
3	10.5	6.6	9.7	100
4	10.6	6.4	10.1	100
5	10.2	4.7	7.4	92.0
6	10.0	8.2	5.1	98.2
7	9.9	7.7	5.1	100
8	10.0	8.2	6.2	100
9	10.0	8.1	9.9	100
10	10.0	7.0	10.1	100
11	10.2	5.6	11.4	100
12	10.1	4.2	10.4	85.3
13	10.1	4.7	9.7	63.0
14	9.3	8.4	2.9	54.2
15	10.6	5.7	6.0	100
Comparative example	10.2	5.8	6.7	16.7

Also, the relationship between the amount (wt%) of sodium trimetaphosphate to add relative to theoretical yield of calcium carbonate and the vaterite ratio is shown in Fig. 1. Figure 2 and Fig. 3 are plots showing the results of X-ray diffraction of the embodiments 1 and 4, respectively. Also, Fig. 4 is a differential thermal analysis (DTA) curve and a weight change (TG) curve of the spherical calcium carbonate obtained in the embodiment 2. The heat generation at 420°C seen in the DTA curve is believed to be due to transformation from vaterite to calcite.

[0029]

Figure 5 ~ Fig. 19 are electron microscope photos of spherical calcium carbonates obtained in the embodiments 1~15, and Fig. 20 is an electron microscope photo of spherical calcium carbonate obtained in the comparative example. Also, the spherical calcium carbonate obtained in the embodiment 2 was left in the air at the room temperature (about 25°C) and its stability was examined. The results are listed in Table 2. Also, an electron microscope photo of the calcium carbonate after 120 days passed is shown in Fig. 21. Note that the magnifications of the electron microscope photos are all 1000 times.

[0030]

From these embodiments and comparative example, it becomes evident that spherical calcium carbonate can be obtained through a reaction under the existence of a specified amount of a specific phosphate compound. Also, spherical calcium carbonate is stable in the air and is not easily transformed to the calcite form, etc.

[0031]

[Efficacy of the Invention]

The spherical calcium carbonate of the present invention has an efficacy that it is stable in the air, its spherical particle shape can be maintained over a long period, therefore it is excellent in characteristics of dispersibility, fillability, smoothness, extendability, polishability, paintability, spreadability, etc., and can be used preferably as an additive or filler.

[0032]

Also, the manufacturing method of the spherical calcium carbonate of the present invention has an efficacy that spherical calcium carbonate can be easily manufactured by reacting calcium chloride and hydrogen carbonate and/or carbonate under the existence of a specified amount of a specific phosphate compound.

[Brief Explanation of Drawings]

[Fig. 1]

A plot showing the relationship between the added amount of sodium trimetaphosphate (wt%) relative to theoretical yield of generated calcium carbonate and the vaterite ratio.

[Fig. 2]

A plot showing the result of an X-ray diffraction of the embodiment 1.

[Fig. 3]

A plot showing the result of an X-ray diffraction of the embodiment 4.

[Fig. 4]

A plot showing the differential thermal analysis curve and weight change curve of the spherical calcium carbonate obtained in the embodiment 2.

[Fig. 5]

An electron microscope photo showing the particle structure of the spherical calcium carbonate obtained in the embodiment 1.

[Fig. 6]

An electron microscope photo showing the particle structure of the spherical calcium carbonate obtained in the embodiment 2.

[Fig. 7]

An electron microscope photo showing the particle structure of the spherical calcium carbonate obtained in the embodiment 3.

[Fig. 8]

An electron microscope photo showing the particle structure of the spherical calcium carbonate obtained in the embodiment 4.

[Fig. 9]

An electron microscope photo showing the particle structure of the spherical calcium carbonate obtained in the embodiment 5.

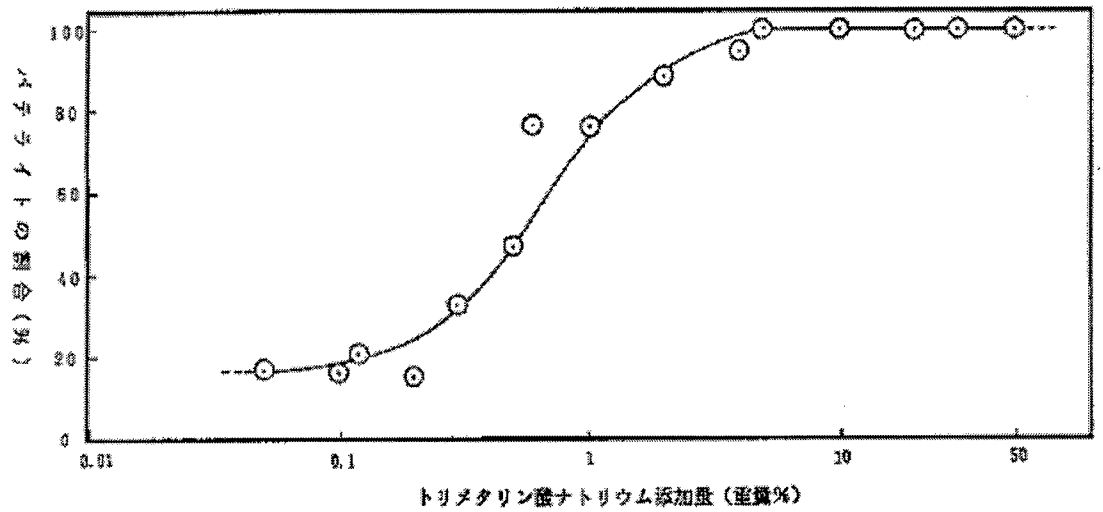
[Fig. 10]

An electron microscope photo showing the particle structure of the spherical calcium carbonate obtained in the embodiment 6.

[Table 2]

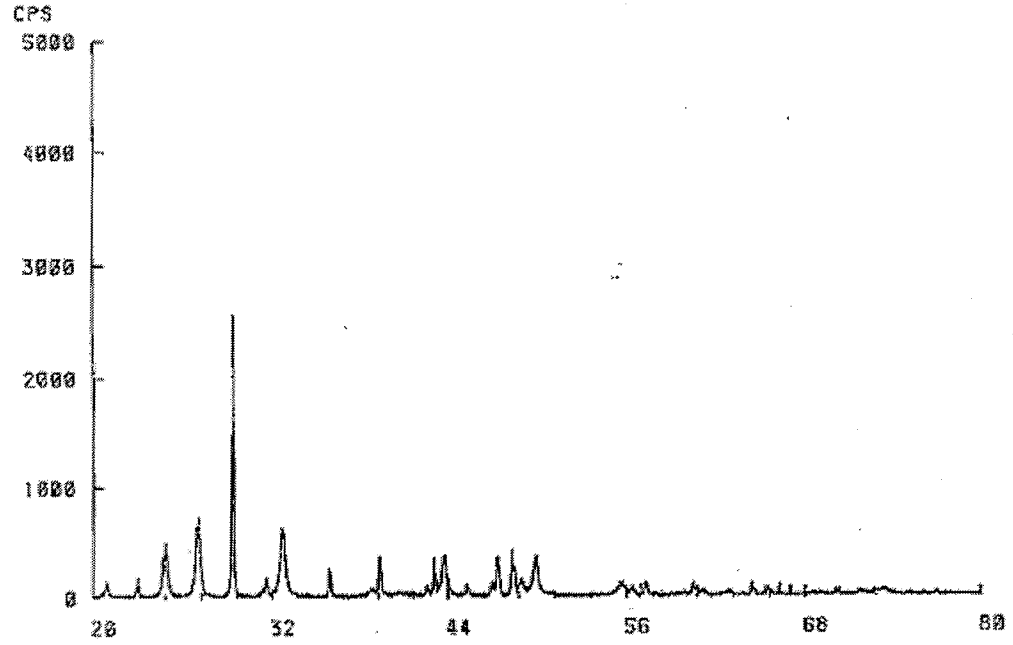
Days passed	Average particle size (μm)	Specific surface area (m^2/g)	Vaterite ratio (%)
0	5.8	5.8	77.0
60	5.9	5.5	74.1
120	6.0	5.6	76.2

[Fig. 1]



(Horizontal axis) Amount of sodium trimetaphosphate added (wt%)
(Vertical axis) Vaterite ratio (%)

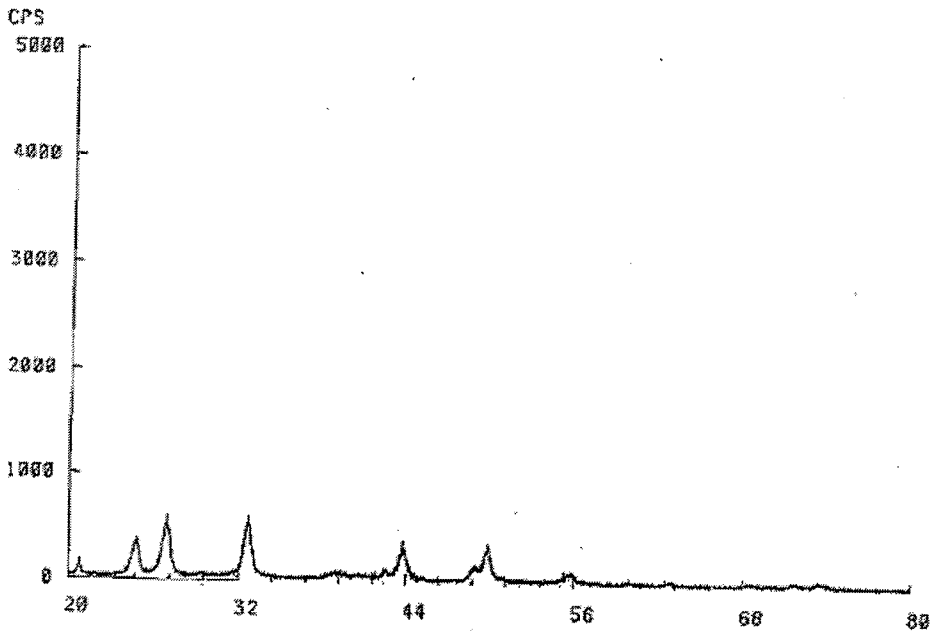
[Fig. 2]



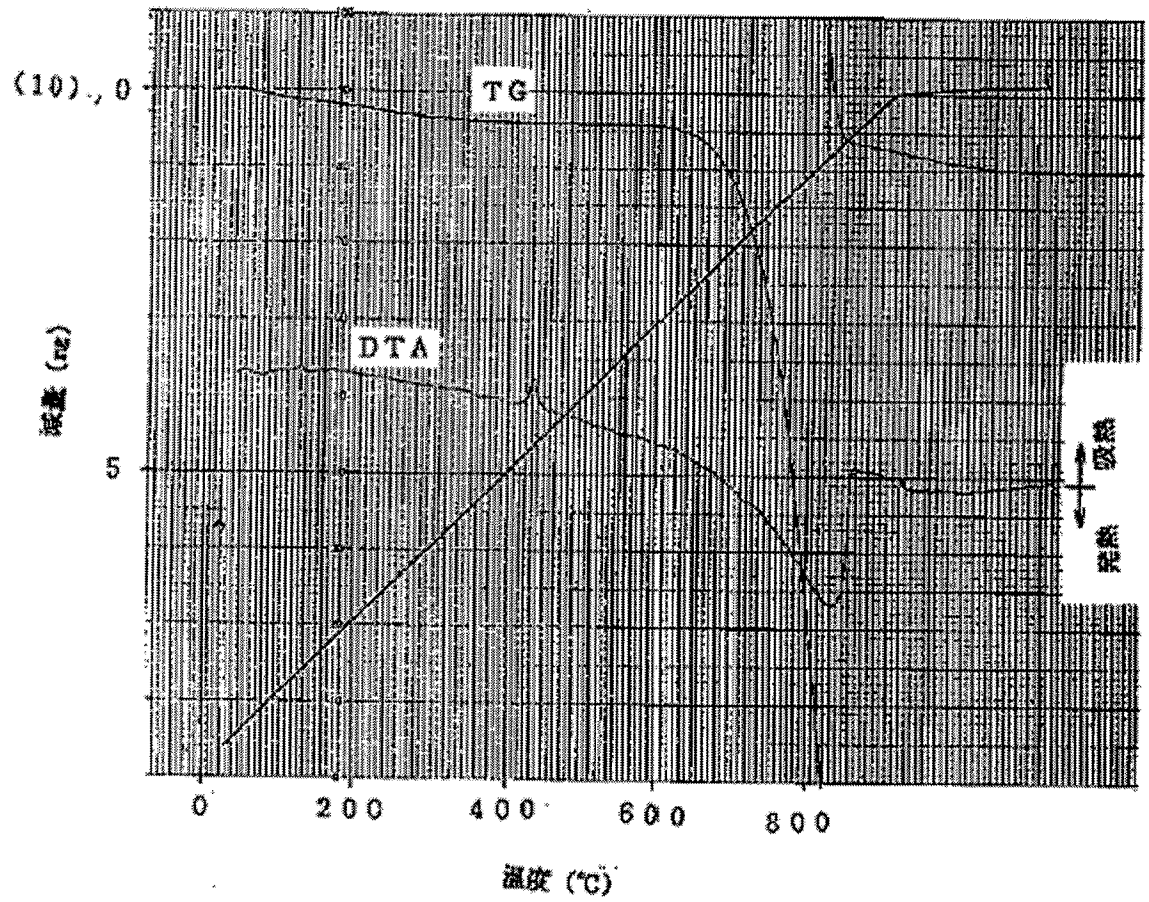
[Fig. 5]
A photo in place of a drawing

[Fig. 6]
A photo in place of a drawing

[Fig. 6]



[Fig. 4]



(Horizontal axis) Temperature (°C)
(Vertical axis) Amount decreased (mg)
(Downward arrow) Heat generation
(Upward arrow) Heat absorption

[Fig. 7]
A photo in place of a drawing

[Fig. 8]
A photo in place of a drawing

[Fig. 9]
A photo in place of a drawing

[Fig. 10]
A photo in place of a drawing

[Fig. 11]
A photo in place of a drawing

[Fig. 12]
A photo in place of a drawing

[Fig. 13]
A photo in place of a drawing

[Fig. 14]
A photo in place of a drawing

[Fig. 15]
A photo in place of a drawing

[Fig. 16]
A photo in place of a drawing

[Fig. 17]
A photo in place of a drawing

[Fig. 18]
A photo in place of a drawing

[Fig. 19]
A photo in place of a drawing

[Fig. 20]
A photo in place of a drawing

[Fig. 21]
A photo in place of a drawing